(19) Japanese Patent Office (JP)

(12) Publication of Laid-Open Patent Application (A)

(11) Publication Number: 6-289210

(43) Date of Publication Application: October 18, 1994

(51) Int. Cl.[5] Identification Mark FI

G02B 5/20 101 8507-2K

Request for Substantive Examination: not requested

Number of Claims: 1 OL

(Total 6 pages)

(21) Application Number:

Japanese Patent Application No. H5-76763

(22) Filing Date: April 2, 1993

(71) Applicant: 000004455

Hitachi Chemical Co., Ltd.

2-1-1, Nishi-Shinjuku, Shinjyuku-ku, Tokyo

(72) Inventor: Yasuki Mori

c/o Hitachi Chemical Co., Ltd.

Yamazaki factory

4-13-1, Higashi-cho, Hitachi-shi, Ibaraki

(72) Inventor: Eiji Fujita

c/o Hitachi Chemical Co., Ltd.

Yamazaki factory

4-13-1, Higashi-cho, Hitachi-shi, Ibaraki

(74) Attorney: Patent Attorney, Kunihiko Wakabayashi

(54) [Title of the Invention]

Manufacturing Method of Color Filter

(57) [Abstract]

[Purpose]

To manufacture a color filter which has a multi-colored minute pattern with a

uniform thickness, high definition, and high heat resistance over a substrate, with a photosensitive film which has good followability and workability.

[Structure]

In a method of manufacturing a color filter, a method of forming a multi color pattern comprising the steps being carried out repeatedly of: attaching a photosensitive film formed of a base film and a single-colored photosensitive resin layer to a transparent substrate so that a colored photosensitive resin layer is in contact with the substrate, forming a predetermined pattern by a light exposure, and peeling off the base film and developing; wherein a base layer of a photosensitive resin containing 0.1 to 30 wt% of a fine-grain metal oxide is preformed over a surface of the substrate.

[Claim]

[Claim 1]

In a method of manufacturing a color filter, a method of forming a multi color pattern comprising the steps being carried out repeatedly of:

attaching a photosensitive film formed of a base film and a single-colored photosensitive resin layer to a transparent substrate so that a colored photosensitive resin layer is in contact with the substrate,

forming a predetermined pattern by a light exposure, and

peeling off the base film and developing;

wherein a base layer of a photosensitive resin containing 0.1 to 30 wt% of a fine-grain metal oxide is preformed over a surface of the substrate.

[Description of the Invention]

[0001]

[Industrial Field of the Invention]

The present invention relates to a manufacturing method of a color filter.

[0002]

[Prior Art]

A color filter is a thing in which extremely minute stripe patterns or mosaic

patterns having two or more kinds of hues are aligned to be parallel or crossed with a certain interval on a surface of a substrate formed from a translucent material such as glass. The patterns are required to have hues which are orderly aligned with a predetermined order and a predetermined interval, and to have a uniform thickness with little unevenness. Various manufacturing methods of forming a color filter are suggested. For example, a color filter can be formed at a low cost by a screen printing method. There is also a method using a photolithography technique in which a transparent film provided on a substrate for a color filter is irradiated with ultraviolet light through a predetermined negative mask, and then a part which is not exposed to light is removed, and the remained parts are dyed while forming a resist printing layer.

[0003]

As an improved method of the foregoing methods, a method in which a colored solution of a photosensitive resin composition is applied to a substrate, dried, exposed to light, and developed to form a pattern of one color; then the same process is repeated repeating to form a pattern of another color to form a color filter can be nominated. There is a known manufacturing method of a color filter in which a multi-colored minute stripe or mosaic pattern can be easily formed by using a photosensitive film formed from a base film and a photosensitive resin layer which are generally used for an etching resist, a plating resist, a solder resist, or the like when manufacturing a printed wiring board. A multi color pattern for manufacturing a color filter is formed by repeating the steps of attaching a photosensitive film formed of a base film and a single-colored photosensitive resin layer to a transparent substrate so that a colored photosensitive resin layer is in contact with the substrate, forming a predetermined pattern by a light exposure, and peeling off the base film and developing. For example, there is a method of forming a pattern in which a photosensitive resin layer containing a colorant of a single color is applied to a support medium and dried to form a photosensitive film; then the photosensitive resin layer of the photosensitive film is transferred to a transparent plate and exposed to light through a mask with a predetermined pattern and then developed to form a pattern (Japanese Patent Application Laid-Open No. S61-99102). Alternatively,

there is a method of manufacturing a pattern of a color filter in which the film is exposed to light through a mask with a predetermined pattern and developed to form a pattern, and then transferred to a transparent plate to form a pattern of a color filter (Japanese Patent Application Laid-Open No. S61-99103). There is also a method in which a pattern for a color filter in which the film is bonded by thermocompression to a transparent plate and exposed to light through a mask with a predetermined pattern, and then a base film is peeled off and developed to form a translucent colored image pattern (Japanese Patent Application Laid-Open No. S63-187203). There is also another method of manufacturing a pattern of a color filter in which the method disclosed in Japanese Patent Application Laid-Open No. S63-187203 is applied except that a photosensitive film is provided with an adhesive medium of polyvinyl acetate copolymer over a color photosensitive resin (Japanese Patent Application Laid-Open No. H02-24624).

[0004]

[Problem to be Solved by the Invention]

In the conventional manufacturing methods, when forming a second or rest of the layer, a step is formed between a color layer which is formed over a first color layer which is already formed and a color layer which is formed directly over the substrate. The step depends on a thickness of the formed color layer (1 to 5 μm). Because of the step, a newly formed color layer is not in contact with a base (transparent glass) and adhesive pressure is not enough, and so adhesive force is not enough, accordingly, a color layer is not bonded to the base. Therefore, when peeling off the base film, a part of the color layer is also peeled off together with the base film, and so a part where the color layer is not bonded to the base is generated. If light-exposure and development of the base in this state is performed, a problem arises that a part where a color image does not exist is also exposed, and so a desired color filter can not be obtained. The present invention provides a manufacturing method of a color filter without the foregoing defect and with improved workability, a high precision, and a multi-color minute pattern.

[0005]

[Means for Solving Problem]

The present invention relates to a method of manufacturing a color filter in which a method of forming a multi color pattern comprises the steps being carried out repeatedly of: attaching a photosensitive film formed of a base film and a single-colored photosensitive resin layer to a transparent substrate so that a colored photosensitive resin layer is in contact with the substrate, forming a predetermined pattern by a light exposure, and peeling off the base film and developing; wherein a base layer of a photosensitive resin containing 0.1 to 30 wt% of a fine-grain metal oxide is preformed over a surface of the substrate.

[0006]

A photosensitive film used in the present invention is a color photosensitive resin layer formed by applying a single-colored photosensitive resin composition over a transparent base film such as a film formed from polyethylene terephthalate to be dried. The color photosensitive resin layer is not hardened, is flexible and having an adhesive property. Therefore, it is preferable to attach a protective film such as a polyethylene film thereover to prevent damage from the outside and a foreign material being attached. The color photosensitive resin layer formed over the photosensitive film is bonded to a transparent substrate while the protective film was peeled off from the photosensitive resin film. The base film on the surface of the color photosensitive resin layer is removed after being exposed to light through a negative mask with a predetermined pattern.

[0007]

A photosensitive resin layer containing 0.1 to 30 wt% of fine-grain metal oxide is preformed over a surface of the substrate. Thereby followability of the film and adhesion of the single-colored photosensitive resin layer are improved. When the base film is peeled off, the photosensitive resin layer is prevented from being peeled off from the substrate, and the photosensitive resin layer is prevented from being peeled off from the substrate when development is carried out.

[0008]

A base layer is formed over a transparent substrate by stacking a photosensitive

resin layer containing fine-grain metal oxide, or by a spin coating method or a dip coating method using a photosensitive resin solution containing the fine-grain metal oxide. As an example of fine-grain metal oxide contained in a photosensitive resin layer for forming the base layer, an antimony trioxide, a magnesium oxide, a zinc oxide, a silicon oxide, or the like can be nominated. An amount of the fine-grain metal oxide to be added is 0.1 to 30 wt%, preferably, 0.1 to 5 wt%. When an amount the fine-grain metal oxide is less than 0.1 wt%, the sufficient effect on improvement of adhesion of an image can not be obtained, and when an amount thereof is more than 30 wt%, the photosensitive resin layer is discolored and transparency thereof is deteriorated. The fine-grain metal oxide preferably has a size from 0.01 to 0.2 μm on average.

[0009]

The single-colored photosensitive resin layer preferably contains ethylene unsaturated compound (a), film forming polymer containing carboxyl group (b), photoinitiator or photoinitiator compound (c) or (d), or pigment or dye (d) and preferably has a thickness of 0.5 to 15 μm.

[0010]

As an example of ethylene unsaturated compound ((a) component), a compound obtained by adding α,β-unsaturated carboxylic acid to polyhydric alcohol, such as trimethylolpropanedi(meta)acrylate (which refers to metaacrylate and acrylate hereinafter), trimethylolpropanetri(meta)acrylate, tetramethylolmethanetri(meta)acrylate, dipentaerythritolpenta(meta)acrylate, dipentaerythritolhexa(meta)acrylate, or the like; or a compound obtained by adding α,β-unsaturated carboxylic acid to glycidyl group-containing compound such as trimethylolpropane triglycidyl ether triacrylate, or bisphenol A diglycidyl etherdi(meta)acrylate, or the like; or esterification derivative of polycarboxylic acid like phthalic anhydride, and a compound containing hydroxy group and unsaturated ethylene group such as β-hydroxyethyl(meta)acrylate or the like; or alkyl ester of (meta)acrylic acid (which refers to meta acrylic acid and acrylic acid hereinafter) such as (meta)acrylic acid methyl, (meta)acrylic acid ethyl, (meta)acrylic acid butyl, and (meta)acrylic acid2-ethylhexyl can be nominated. Alternatively, urethane diacrylate

compound which can be obtained by reaction of trimethylhexamethylene diisocyanate, dihydric alcohol, and divalence(meta)acrylic acid monoester may be used. Two or more kinds of the foregoing compounds may be used. The blending amount of (a) component is preferably 90 to 50 parts by weight, if the total amount of (a) component and (b) component is assumed to be 100 parts by weight.

[0011]

As an example of film forming polymer containing carboxyl group ((b) component), copolymer of (meta)acrylic acid alkyl ester and (meta)acrylic acid; copolymer of (meta)acrylic acid alkyl ester, (meta)acrylic acid, and vinyl monomer which can form copolymer with the foregoing two materials can be nominated. As an example of (meta)acrylic acid alkyl ester, (meta)acrylic acid methyl, (meta)acrylic acid ethyl, (meta)acrylic acid butyl, and (meta)acrylic acid 2-ethylhexyl can be nominated. As an example of (meta)acrylic acid alkyl ester, (meta)acrylic acid, and vinyl monomer which can form copolymer with the foregoing materials, (meta)acrylic acid dimethylethyl, (meta)acrylic acid tetrahydrofurfuryl, (meta)acrylic acid diethyl, 2,2,2-trifluoroethyl(meta)acrylate, 2,2,3,3-tetrafluoropropyl(meta)acrylate, acrylamide, diacetone acrylamide, styrene, vinyl toluene, can be nominated. Alternatively, polyester including (meta)acrylic acid as copolymer component such as terephthalic acid, isophthalic acid, and sebacic acid, copolymer of butadiene and acrylonitrile, cellulose acetate, cellulose acetate butyrate, methyl cellulose, ethyl cellulose, or the like can be nominated.

[0012]

By using (b) component, a film coating property and a film property of a hardened material are improved. The blending amount of (b) component is preferably 10 to 50 parts by weight, if the total amount of (a) component and (b) component is assumed to be 100 parts by weight. There is a tendency that optical sensitivity is decreased due to an increase of ethylene unsaturated compound when the blending amount is less than 10 parts by weight, and a photo curing material becomes brittle when the blending amount is more than 50 parts by weight. The weight-average molecular

weight of (b) component is preferably more than 10,000 in terms of the film coating property and a film strength.

[0013]

As an example of photoinitiator or photoinitiaor compound ((c) component), aromatic ketone such as benzophenone, N,N'-tetramethyl-4,4'-diaminobenzophenone (Michler's ketone), N,N'-tetramethyl-4,4'-diaminobenzophenone, 4-methoxy-4'-dimethylaminobenzophenone, 4,4-diethylaminobenzophenone, 2-ethylanthraquinone, or phenanthrenequinone; benzoin such as benzoin ether like benzoin methyl ether, benzoin ethyl ether, or benzoin phenyl ether, or methyl benzoin, or ethyl benzoin; 2,4,5-triarylimidazole dimer such as 2(o-chlorophenyl)-4,5-diphenylimidazole dimer, 2-(o-chlorophenyl)-4,5-di(m-methoxyphenyl)-4,5-diphenylimidazole dimer, 2-(o-fluorophenyl)-4,5-diphenylimidazole dimmer, 2-(o-methoxyphenyl)-4,5-diphenylimidazole dimmer, 2,(p-methoxyphenyl)-4,5-diphenylimidazole dimmer, 2,4-di(p-mexiphenyl)-5-phenylimidazole dimmer, 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazole dimmer, and 2-(p-methylmerrcapto phenyl)-4,5-diphenylimidazole dimmer can be nominated.

[0014]

The blending amount of (c) component is preferably 0.1 to 10 parts by weight, if the total amount of (a) component and (b) component is assumed to be 100 parts by weight. There is a tendency that optical sensitivity is not enough when the blending amount is less than 0.1 parts by weight, and light absorption of the surface is increased and photo curing in the inside is not performed sufficiently when the blending amount is more than 10 parts by weight.

[0015]

As an example of pigment or dye ((d) component), a known colorant can be used. The colorant is chosen in terms of a compatibility with a component of a photosensitive resin layer, specifically ethylene unsaturated compound or film forming polymer

containing carboxyl group; a target hue; a light-transmitting property; and the like. The blending amount of (d) component is preferably 1 to 20 parts by weight, assuming that the total amount of (a) component and (b) component is 100 parts by weight. There is a tendency that coloring is not performed sufficiently when the blending amount is less than 1 part by weight, and a light-transmitting property is decreased when the blending amount is more than 20 parts by weight.

[0016]

A color photosensitive resin layer preferably contains a melamine resin and/or an epoxy resin which initiate/initiates a thermal reaction with a carboxyl group contained in film forming polymer containing carboxyl group to improve a thermosetting property at 1 to 20 parts by weight of the total amount of (a) component and (b) component which is assumed to be 100 parts by weight. They are added and heated at a temperature of 130 to 200 °C for 30 to 60 minutes, thereby cross-linking intensity of the color layer is improved, and a heat resistance is increased significantly.

[0017]

In the case of using a glass plate as a substrate in a color filter, it is preferable to use a glass plate which is pretreated with a silane coupling agent to improve an adhesion between a color photosensitive resin layer and a glass plate. Alternatively, an adhesion between a photosensitive resin layer and a glass plate can be enhanced by adding a silane coupling agent to a color photosensitive resin layer. An amount of the added silane coupling agent is 1 to 30 parts by weight of the total amount of (a) component and (b) component which is assumed to be 100 parts by weight.

[0018]

In the present invention, a color filter is manufactured as follows. First, a color photosensitive resin layer formed on a photosensitive film is pasted on a transparent substrate to be exposed to light with a negative mask having a predetermined pattern over a base film on the surface of the color photosensitive resin layer. After that, the base film is removed. Then, the part which is not exposed to light is developed using a developing solution to form a color pattern. The process of forming a color pattern is

repeated predetermined times using a photosensitive film of a different color to form a pattern of another color thereby a color filter is formed.

[0019]

[Example]

Example 1

1) Manufacturing a photosensitive film

5 parts by weight of any one of pigments in Table 2, 5 parts by weight of a melamine resin, and 5 parts by weight of a silane coupling agent were added to and dissolved in 206 parts by weight of a solution A in which the materials in Table 1 were dissolved uniformly to obtain a solution for forming a photosensitive resin layer.

[Table 1]

Material	Blending Amount
A reactant of trimethylhexamethylene diisocyanate/ 1,4-cyclohexanedimethanol/ 2-hydroxyethyl acrylate (equivalent ratio of 16:5:8)	55 parts by weight
A copolymer of methyl methacrylate/ methacrylic acid/2-ethylhexyl acrylate (weight ratio of 60:20:20)	45 parts by weight
A mixture of benzophenone and 4,4'-diethylamino benzophenone (weight ratio of 20:1)	6 parts by weight
Methyl ethyl ketone	70 parts by weight
Propylene glycol monomethyl ether	30 parts by weight

[Table 2]

<Pigment>

Colortex Red UEM (manufactured by Sanyo Color Works. Ltd) (red)
Colortex Blue UEM (manufactured by Sanyo Color Works. Ltd) (blue)
Colortex Green UE-1203 (manufactured by Sanyo Color Works. Ltd) (green)
Colortex Black USM (manufactured by Sanyo Color Works. Ltd) (black)

As a melamine resin, Cymel 300 (hexamethoxymethyl 50, a trade name of melamine, manufactured by Mitsui Toatsu Chemical Co., Ltd.) was used. As a silane coupling agent, K3M503 (manufactured by Shin-Etsu Chemical Co., Ltd.) was used. The obtained solution was applied to have a uniform thickness over a polyethylene terephthalate film having a thickness of 25 μm (manufactured by Teijin Limited. Tetoron film S25), then dried at 100 °C for 2 minutes in a drying machine. A polyethylene film having a thickness of 30 μm was bonded thereto as a protective film to form a photosensitive film. The photosensitive resin layer had a thickness of 2 μm after being dried.

2) Manufacturing a base layer (a base layer which includes 0.3 wt% of a metal oxide)

Materials in Table 3 were compounded and uniformly mixed. The obtained solution was applied to have a uniform thickness over a polyethylene terephthalate film having a thickness of 25 μm (S25), then dried at 100 °C for 2 minutes in a drying machine. A polyethylene film having a thickness of 30 μm was bonded thereto as a protective film to form a photosensitive film. The photosensitive resin layer had a thickness of 2 μm after being dried.

[Table 3]

Material	Blending Amount
A copolymer of methyl methacrylate · methacrylic acid · tetrahydrofurfuryl methacrylate (weight ratio of 78:2:20)	35 parts by weight
A reactant of trimethylhexamethylene diisocyanate · 1-4-cyclohexanedimethanol · 2-hydroxyethyl acrylate (weight ratio of 16:5:8)	65 parts by weight
Irgacure-651 (benzyldimethyl ketal)	5 parts by weight
Antimony trioxide (metal oxide, a size of 0.02 μm on average)	0.3 parts by weight
Methyl ethyl ketone	100 parts by weight
Toluene	40 parts by weight

Next, a glass plate having a thickness of 1 mm was heated at 80 °C for 10

minutes. The color photosensitive resin layer was stacked over the glass plate at a roll temperature 120 °C, a roll pressure 4 kg/cm^2, and a speed of 1.5 m/minutes while a photosensitive film of the polyethylene film was peeled off. Then, after a light exposure with an exposure apparatus HMW-201B (3kW, ultrahigh pressure mercury lamp, manufactured by Orc Seisakusho Co., Ltd.), the polyethylene terephthalate film was removed. Then, emitting light at 3 J/cm^2 with an ultraviolet ray irradiating apparatus (lamp H5600L/2, manufactured by Toshiba Light and Technology Corp.) and heating at 150 °C for 45 hours were carried out to obtain a base substrate for a color filter. Next, the base substrate for the color filter was heated at 80 °C for 10 minutes. The photosensitive resin layer was stacked at a roll temperature 120 °C, a roll pressure kg/cm^2, and a speed of 1.5 m/minutes while the protective film of the foregoing photosensitive film for the color filter manufactured in 1) was peeled off. Then, after a light exposure through a negative mask provided with a predetermined pattern with an exposure apparatus HMW-201B (3kW, ultrahigh pressure mercury lamp, manufactured by Orc Seisakusho Co., Ltd.), the polyethylene terephthalate film was removed. A portion which was not exposed to light was removed by a spray development with a 2 wt% aqueous solution of Na_2CO_3 at 30 °C for 10 to 20 seconds to form a color pattern of one color. The forming process of a color pattern was carried out four times using each of photosensitive films having a color of red, blue, green, and black sequentially, thereby forming a multi-color pattern shown in FIG. 1. The exposure energy was 150 mJ/cm^2 in the cases of photosensitive resin layers of red, blue, and green, and 300 mJ/cm^2 in the case of a photosensitive resin layer of black. The obtained multi-color pattern was irradiated at 3 J/cm^2 with an ultraviolet ray irradiating apparatus (lamp H5600L/2, manufactured by Toshiba Light and Technology Corp.) and heated at 150 °C for 45 minutes to obtain a color filter. The obtained color filter had orderly aligned patterns of red, blue, and green. The gaps between them were filled with black.

Example 2, 3

Base layers were formed with the amount of the metal oxide which was 0.3 wt% contained in the base layer in Example 1 changed to 1.0 wt% or 5.0 wt%. Favorable

color filters like that of Example 1 were obtained.

[0020] Comparative Example 1

As in Example 1, photosensitive films were formed for each pigment of red, blue, green, and black by using a polyethylene terephthalate film having a thickness of 25 μm (manufactured by Teijin Limited. Tetoron film S25) as a base film and a polyethylene film having a thickness of 30 μm which was bonded thereto as a protective film. A color pattern for red was formed without forming a base layer as in Example 1; then, the forming process was carried out three times for each color of blue, green, and black sequentially. A multi-color pattern like that of the example 1 was formed. FIG. 2 is a schematic diagram of the obtained multi-color pattern. The patterns of red (1) which were formed at first were favorable, while the pixels of blue (2) and green (3) were formed only partly at the gaps (325 μm) between the neighboring red pixels. Especially a blue pixel, which was aligned next to a red pixel with an interval of 25 μm was reproduced only to have a width of 50 μm, and a 125 μm square was not reproduced. Black pixel was not formed completely.

[0021]

[Effect of Invention]

According to the manufacturing method of the present invention, a color filter which has a multi-colored minute pattern with a uniform thickness, high definition, and high heat resistance over a substrate, with a photosensitive film which has good followability and workability can be manufactured.

[Brief Description of Drawings]

FIG. 1 is a diagram showing a pattern of a color filter formed in the examples of the present invention; and

FIG. 2 is a diagram showing a pattern of a color filter formed in the comparative example of the present invention.

[Explanation of Reference]

1: red, 2: blue, 3: green, 4: black.